Trends and Developments in C_9-Hydrocarbon Tackifier Resins

Content

This brochure covers trends and developments in C9-hydrocarbon tackifier resins.

Tailor-made EVA-compatible resins
Light-coloured aromatic resins
Resins with low odour
Resins for reactive hot melts
Resins for low VOC water-borne adhesives

Introduction

Resins are often used to improve the tack of an adhesive formulation. They can be classified into

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Kinds of resins

natural resins

- wood rosins
- gum rosins
- tall oil rosins
- and derivatives thereof

synthetic resins

- C_5-resins (aliphatic)
- C_9-resins (aromatic)
- C_5/C_9-resins (aliphatic/aromatic)
- DCPD-resins (cycloaliphatic)
- terpene-resins (cycloaliphatic)
- (partly) hydrogenated resins

Depending on the back-bone polymer being used in the adhesive formulation a special kind of resin is used as a tackifier to improve the properties especially at application temperature. The improvements are due to a defined compatibility of the polymers and resins. The improvements have an influence on tack, viscosity, heat resistance, adhesion, colour etc. of the final adhesive. Back-bone polymers cannot be used alone for many reasons.

As an example, the very high viscosity of the polymers results in an inadequate substrate wetting. In addition the hot tack around the application temperature is too low for most technical requirements for hot melt applications whether structural or pressure sensitive. Therefore, aliphatic C_5-resins or terpene resins are often used as tackifiers for the mid-block of styrenes block copolymers (with an isoprene mid-block) in PSA-formulations or hot melt adhesives based on polyolefins, whereas hot melt adhesives based on EVA (ethylene vinylacetate) copolymers are often formulated with aromatic C_9-resins to improve tack and heat resistance e.g. for woodworking or paper and packaging applications. (Partly) hydrogenated or pure monomer based resins are used where additionally low to no colour of the adhesive is needed, e.g. in the diaper production or for bookbinding application.

Tailor-made Ethylene-Vinylacetate (EVA) compatible Resins

A domain for the use of aromatic C_9- and aliphatically modified C_9-resins is the formulation of EVA-based hot melt adhesives. The action of the resins is

⇒ increase of the hot tack
⇒ control of the melt viscosity
⇒ adjustment of open time
⇒ improvement of the heat resistance

To meet these requirements a defined compatibility of the resin to the EVA back-bone polymer is needed. The resin can act as a non-volatile solvent for the polymer because it has a much lower molecular weight. If resin and EVA show complete compatibility the resulting blend will be transparent and homogeneous. The power of a resin to dissolve the polymer depends on temperature. The cloud point expressed in °C is an indication of the degree of solvency and therefore the compatibility.

Vinylacetate (VA) content of the EVA-copolymer indicating its polarity and polarity of the resin and molecular weight (distribution) of the resin are the crucial properties influencing compatibility, solubility and stability of resins.

The factors that control these properties are

⇒ chemical composition (polarity)
⇒ polymerization process parameters (molecular weight distribution).

In combination with EVA copolymers, aromatic C_9-resins are mainly used for the formulation of hot melt adhesives for paper- and packaging and woodworking applications.

Paper and Packaging

In formulations for paper and packaging applications often semi-crystalline waxes are additionally added to adjust open-time characteristics and setting properties. An example of a typical hot melt is given below.

EVA-based formulation:

30 % EVA
50 % resin
20 % wax
and additives

From this formulation, it can clearly be seen that the resin has an important influence on the hot melt properties. Due to the nature of the substrates to be bonded, paper and packaging hot melts are normally applied at temperatures between 140 and 160°C. For these hot melt formulations, resins with softening points between 100 and 120 °C are mainly in use.
The next diagram demonstrates the influence of the vinylacetate content of the EVA copolymer on the compatibility for different aromatic or aliphatically modified aromatic hydrocarbon resins:

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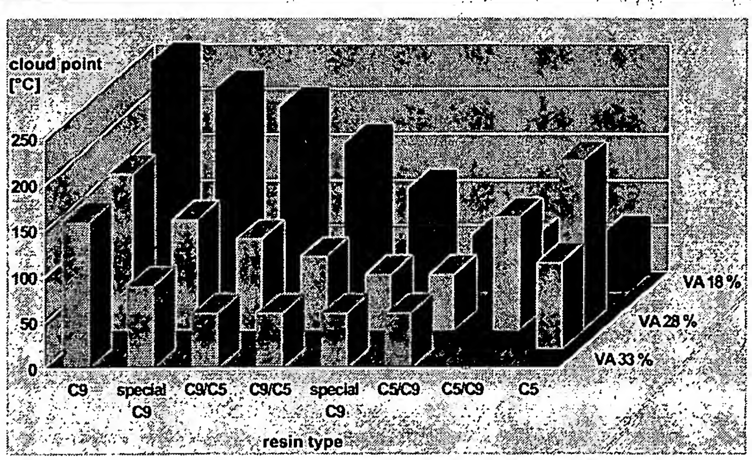
[redacted]



In principle the aromaticity of the resins decreases from the left (pure C_9) to the right (pure C_5). From these results, the following conclusions can be made:

An increase in the aliphatic character of aromatic hydrocarbon resins results in a decrease of the cloud point, therefore the resins become more compatible with the EVA copolymer.
The higher the vinylacetate content, the better is the compatability to the aromatic resins.
For aliphatic hydrocarbon resins, an increase in the aromatic character is accompanied by decreasing cloud points.
For aliphatic resins the compatibility with EVA copolymers becomes better with decreasing amount of vinylacetate in the copolymer.

Not only chemical composition but also softening point of the resin influences the properties of a hot melt adhesive. For a chemically comparable set of a mainly aromatic hydrocarbon resin the influence of the softening point and consequently the molecular weight (distribution) on the compatibility to EVA copolymers is shown in the next two diagrams.

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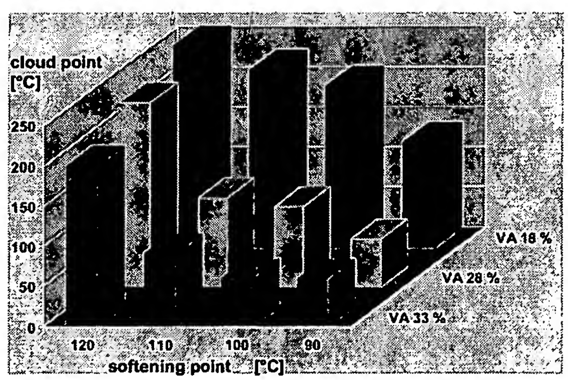
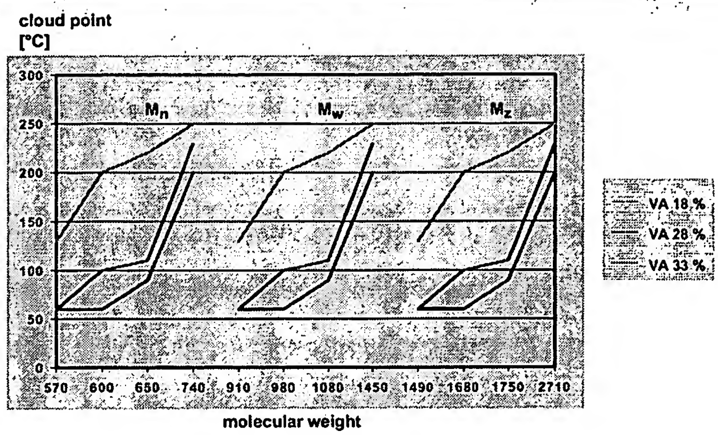
EVA-compatibility of Novares TK series
(ratio 1:1)



EVA-compatibility of Novares TK series
(ratio 1:1)



The diagram above shows that the cloud point within one chemically comparable resin series depends on the molecular weight (distribution) of the hydrocarbon resin. The higher the molecular weight, (represented by the approximate softening point), the higher is the cloud point of the 1:1 mixture with the EVA copolymer. Therefore hot melt adhesive properties are adjustable by choosing different softening point resins.

Novares offers a wide choice of well defined EVA compatible C_9-resins due to a tailor-made production by
⇒ a sophisticated raw material work-up
⇒ selective blending of raw materials
⇒ modifications

Thus the special adhesive requirements can be fulfilled by properly selecting the EVA copolymer and the specific resin to go with it.

Woodworking Hot Melts

A typical formulation for a woodworking hot melt consists of:

EVA-based formulation:
40 % EVA
30 % resin
30 % fillers
and additives

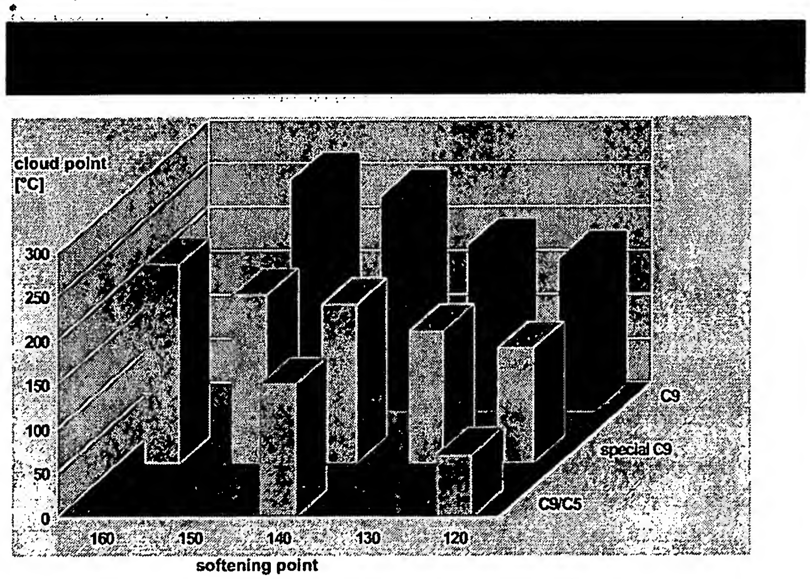
The amount of resin(s) is nearly one third of the formulation which indicates that the resin has an important influence on the hot melt properties.

These hot melt adhesives are applied at temperatures around 180 – 200 °C. Tackifier resins, for example a high softening point hydrocarbon resin, are commonly used to
⇒ increase heat resistance
⇒ adjust open time
⇒ increase adhesion
⇒ improve process efficiency by balancing melt viscosity and EVA-compatibility

For numerous applications in the woodworking industry, for example edge bonding of decorative boards or lamination of chipboard and fibreboard, special aromatic and aliphatically modified aromatic hydrocarbon resins have proven to suit particularly well.

The next picture shows cloud points of standard aromatic and special aromatic hydrocarbon resins as a function of the softening points.

Trends and developments in C_9-hydrocarbon tackifier resins



Some general aspects can be seen:

Higher softening point resins result in higher cloud points of the mixtures.
In general the standard aromatic hydrocarbon resins are less EVA compatible. Thus high amounts of natural resins have to be incorporated to improve compatibility to form a homogenous melt at application temperatures and to reduce melt viscosity. However, a higher concentration of natural resins can have a negative effect on heat resistance of the hot melt because the softening points of these resins are limited to 120 – 130 °C.

Special aromatic resins like NOVARES TN-types that are mainly designed for woodworking applications, show a distinctly lower cloud point and thus improved EVA compatibility compared to standard aromatic resins, even with higher softening points.

Hot melt adhesives with excellent heat resistance and good adhesive performance can be formulated with special NOVARES TN-resins that have unique compatibility properties and high softening points.

Wide choice of aromatic C_9-resins due to a tailor-made production:
⇒ high softening points and therefore a good heat resistance
⇒ excellent EVA-compatibility
⇒ better performance in machine operations due to a reduced build-up

Summarizing the results for woodworking applications, a wide range of tailor-made C_9-tackifier resins is available especially with high softening points for hot melt adhesives based on EVA copolymers. Especially with these special aromatic resins it is possible to produce high quality hot melt adhesives. Due to the excellent EVA compatibility of the hydrocarbon resins, the amount of natural resins can be reduced, yielding formulations that have better heat resistance and better adjustable open times. As a consequence hot melts based on these special C_9-resins show a better performance in machine operations due to reduced build-up of the adhesive on the applicator resulting in a cleaner adhesive application.

Light-coloured Aromatic Hydrocarbon Resins

Improvements in product quality is a permanent process in the adhesive industry as well as for the hydrocarbon resin suppliers. Therefore the suppliers are constantly improving the resin colour. Depending on the amount of resin being used in the final adhesive formulation the resin colour is important. For typical applications like paper and packaging hot melts or PSA adhesive systems amount up to 50 % of a hydrocarbon resin or mixtures of hydrocarbon resins are often used. Here the resin colour determines the adhesive colour. Especially with upcoming unfilled systems this problem becomes more and more important.

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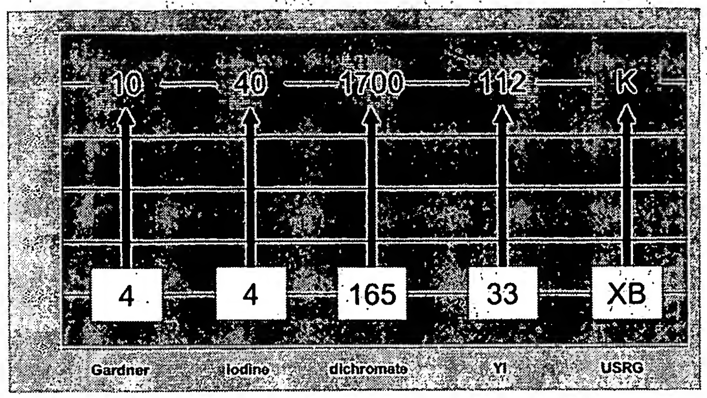
Comparison of color scales



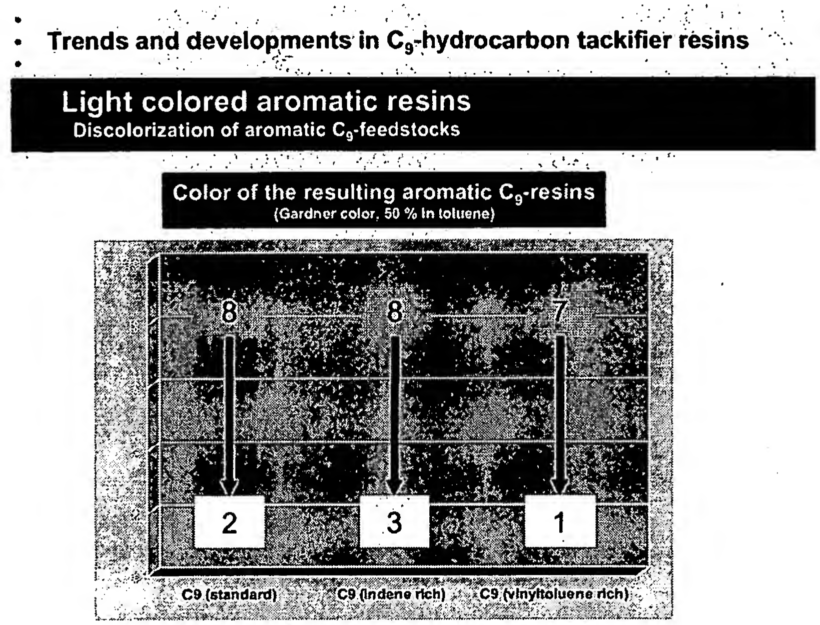
Aromatic hydrocarbon resins normally show colours in the range of 4 up to 9 - 10 according to the Gardner scale in a 50 % toluene solution.

In principle there are three different ways to get lighter-coloured aromatic resins:
⇒ partial hydrogenation of the resin
⇒ pure monomer-based resins
⇒ discolourization of the feedstock

Hydrogenation is an effective method to reduce colour. It is often used to get fully hydrogenated hydrocarbon resins coming from both aliphatic as well as aromatic raw material feedstocks. Since such products do not contain any aromaticity these resins can be seen as aliphatic or cycloaliphatic hydrocarbon resins. But also partial hydrogenation is possible with aromatic resin material. By balancing the degree of hydrogenation light to water-white resins can be produced containing both mixed aliphatic or cycloaliphatic as well as aromatic structures to maintain the required resin properties. In this way very light resins are available for tackifying the midblocks of block copolymers that also have good compatibility to polyolefins and EVA copolymers. They can be used for e.g. packaging, non-wovens applications, and the production of glue sticks.

Very light to water-white resins can be produced from pure monomer feedstocks. These resins are normally composed of styrene and α-methylstyrene. Pure vinyltoluene feedstocks are used as well. Low polymerization temperatures down to 0 °C have to be applied to get resins with softening points of 100 °C and higher. The need for advanced equipment results in higher costs for the production of these resins. They are used in PSA and hot melt adhesives, sealants and caulking compounds. They also act as reinforcer for endblocks of styrenic block copolymers.

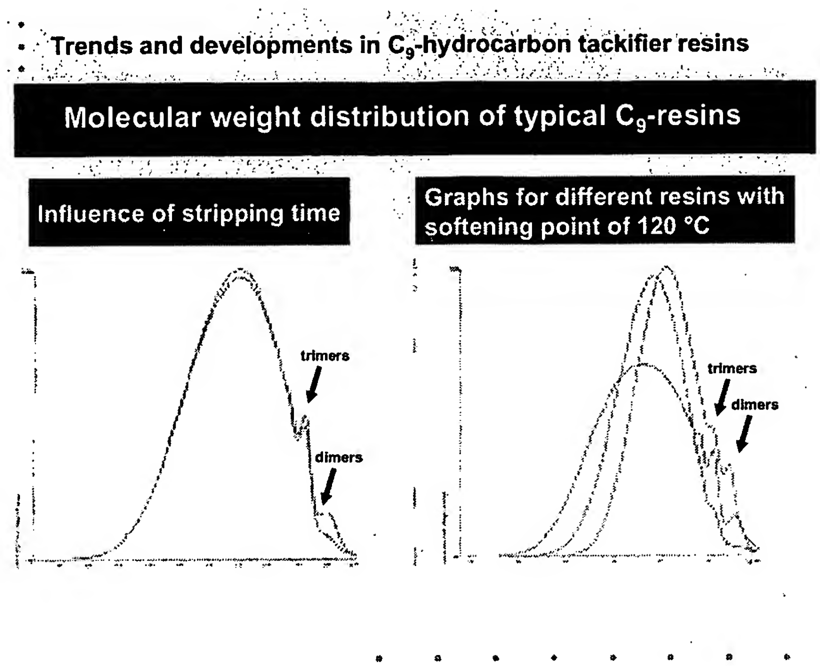
Another way to get light-coloured aromatic hydrocarbon resins is the discolourization of the raw material feedstock. Different methods are described in the patent literature, e.g. to discolourize by using acid clay, maleic acid anhydride etc.



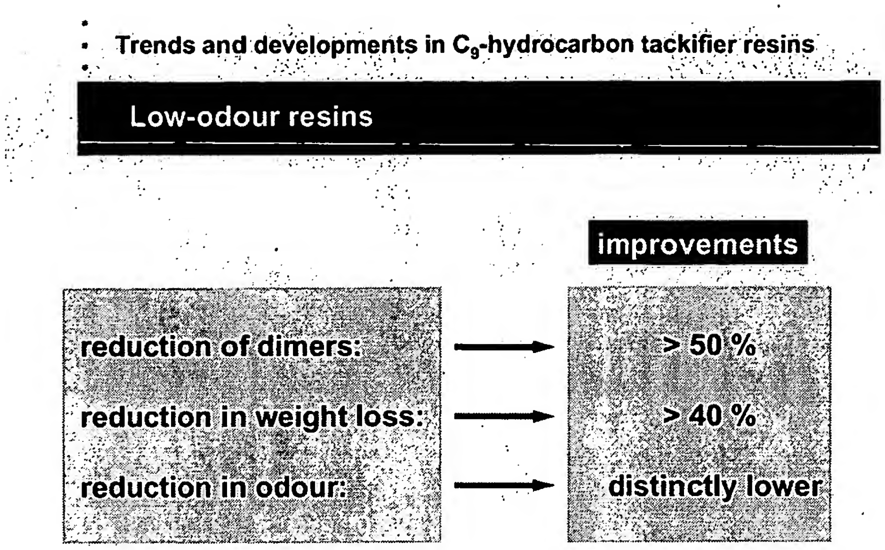
Although starting with a nearly water-white aromatic C_9-hydrocarbon resin feedstock the catalytic polymerization ends in a resin with a Gardner colour of 1 - 3 depending on the raw material composition. All other properties like viscosity, acid number and especially compatibilities to backbone polymers being the same discolourized these resins are fully comparable to their normal counterparts. Therefore, light coloured aromatic C_9-hydrocarbon resins can be produced with the resin profiles of standard resins at relatively low cost.

Resins with low Odour

One aspect becoming more and more important is the reduction of odour of hydrocarbon resins.



Looking at the molecular weight distribution different amounts of dimers and trimers can be seen. In the right picture, molecular weight distributions for typical aromatic C_9-resins are shown all having a softening point of 120 °C. The required softening point has to be met by direct polymerization as far as possible, otherwise the resin has to be fluxed with low molecular weight material leading to higher degrees of odour. It is technically possible to improve the process design to achieve a more effective evaporation of lower boiling components still being present in a hydrocarbon resin even with higher softening points. This will reduce the amount of weight loss and along with that reduce the odour of resins to a technically possible extent.



In pilot plant tests we succeeded in reducing the amount of dimers in a range of above 50 % and the weight loss above 40 %. As it was tested by a group of experts in sensoric investigations the odour of these resins is distinctly reduced compared to that coming from normal production facilities.

Resins for reactive Hot Melts

Some solvent based adhesives have been replaced by other technologies. E.g. water-borne adhesives are used in flooring. Thermoplastic hot melt adhesives are used in the woodworking and shoe industries and reactive hot melt adhesives are used in construction, woodworking, paper and packaging, textile and automobile applications.

The advantages of thermoplastic adhesives are fast set times, good green strength and simple, clean processing. The disadvantages are relatively high application temperatures and limited heat resistance. Chemically reactive adhesives have poor green strength and take time to set. Once cured, the reactive adhesives have greater cohesion and better heat resistance.

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Advantages/disadvantages of reactive adhesive systems

	Advantages	Disadvantages
Thermoplastic adhesive	• setting time • green strength • processing	• application temperature • heat resistance
Reactive adhesive	• heat resistance • cohesion	• defined ratio of two reactants • green strength

The advantages of both the thermoplastic adhesives as well as the reactive adhesives are combined in reactive hot melt systems. Non-reactive, aromatic hydrocarbon resins are used in these reactive, hot melt adhesives, for example in PUR-Hotmelts.

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Compatibility of aromatic C_9-resins to copolyesters

	Dynacoll®- Copolyester															
	7130		7150		7220		7230		7250		7321		7360		7380	
ratio	7:3	9:1	7:3	9:1	7:3	9:1	7:3	9:1	7:3	9:1	7:3	9:1	7:3	9:1	7:3	9:1
Novares-Resin TK 100	IS	IS	NC	NC	NC	CM	IS	NC	IS	IS	NC	NC	NC	NC	CM	CM
Novares-Resin TM 90	IS	IS	NC	NC	IS	NC	IS	NC	NC	NC	NC	NC	IS	IS	NC	NC
Novares-Resin TN 100	IS	IS	NC	NC	CM	CM	IS	IS	IS	IS	IS	NC	NC	CM	CM	CM
Novares-Resin TNA 120	IS	IS	NC	NC	CM	CM	CM	CM	CM	CM	CM	IS	CM	CM	CM	CM
Novares-Resin TS 120	IS	IS	NC	NC	CM	CM	IS	IS	IS	IS	NC	NC	CM	CM	CM	CM

IS: incompatibility/separation NC: no separation/cloudiness CM: clear melt

Copolyesters of the three groups of the Dynacoll® 7000-series, 7100, 7200 and 7300, are designed as building blocks for the production of moisture-curable hot melt adhesives. The properties of such reactive hot melts can be tailor-made within a broad range by blending of two or more copolyesters to achieve the required properties, e.g. open time, viscosity, cohesion and adhesion. Due to the defined compatibility of the aromatic hydrocarbon resins to the different types of copolyesters aromatic hydrocarbon resins are used as modifiers for reactive hot melt systems. The use of such a hydrocarbon resin positively influences the adhesive properties by

⇒ increase of the initial tack
⇒ increase of the hydrophobicity
⇒ increase of the green strength by adjusting the crystallization behaviour.

There are several different copolyester types (amorphous, liquid, crystalline) to comply for specific adhesive requirements. Several highly compatible aromatic hydrocarbon resins can be choosen as well. Therefore all kinds of aromatic hydrocarbon resins are used in reactive hot melt systems, e.g. pure monomer-based resins, aliphatically modified aromatic resins and especially phenolic modified aromatic resins with high resin polarity and therefore showing the best compatibility to polar copolyester systems.

Resins for low volatile organic compounds (VOC) containing Dispersion Adhesives

Water-borne adhesives are often used as flooring adhesives. They are generally composed of a polymer dispersion and a tackifier system as functional components. Until now, highly concentrated rosin (or rosin derivatives) solutions in low boiling solvents or expensive water-dispersed rosin esters have been widely used as tackifiers. For reasons of occupational health and safety it became vital to replace these low boiling solvents, partially or completely. The function of the solvent of the tackifier solution in a dispersion adhesive was the following:

facilitation of blending the solid tackifier resin into the polymer dispersion
soaking the polymer for an easy diffusion of the tackifier resin into the polymer particles
temporary plasticizer
regulation of the open time (to a certain extent)

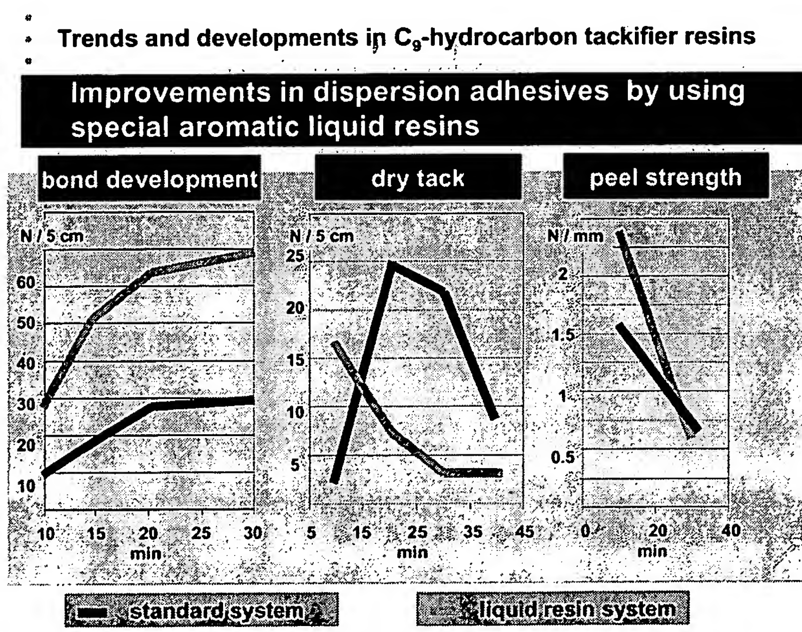
Low boiling solvents were replaced by high boiling plasticizers to carry the tackifiers into the polymer matrices. But this new generation of flooring adhesives, however, show a drawback which becomes evident in time and is also apparent during application: an intensive unpleasant odour. This has led, particularly in the German market, to a growing number of complaints about smell. The suspected possible cause was the plasticizer. Investigations showed that despite their high boiling point of above 200 °C they were released relatively quick into the atmosphere at ambient temperatures. Further investigations indicated that the plasticizers were potentially harmful. This motivated the adhesive industry in Germany to find alternatives.

A solution for this problem is an adjusted system of polymer dispersion, tackifier resin and tailor-made special liquid hydrocarbon resin. In such fine-tuned systems, a 1:1 resin mixture of a solid rosin and a special aromatic liquid resin is used as a tackifier system. The adhesive effect is produced directly from the interaction of the polymer with the resins used in the formulation. In contrast to conventional plasticizers, this special aromatic liquid resin is a dissolving intermediary in liquid resin form that can be used with tested rosins. These special resins, e.g. NOVARES® LS 500, are low in viscosity and specifically developed for use in low emission adhesive systems.

The NOVARES® LS 500 solves the odour problem and improves the adhesive system as follows:

⇒ VOC-content < 500 µg/m³
⇒ bond development
⇒ peel strength

In comparison to solvent or plasticizer containing formulations the TVOC level of the adhesive is only increased by the comparatively low level of VOC from this resin and not by the total amount of resin. Independent test laboratories confirmed that the VOC level is < 500 µg/m³.



In these diagrams the new water-borne adhesive system based on the tackifier mixture with the special aromatic liquid resin, called liquid resin system, is compared to a plasticizer system with good technical results in a basic standard formulation.

It is shown that the open time for the new system is shorter than for the standard system. Dry tack is improved only for short times but this can be adjusted in real adhesive formulations. Peel strength is improved since there are only very low levels of fugative materials to interfere with the bond development. The bond development of the new water-borne adhesive is distinctly better than for the standard adhesive system. Although the key to these improved adhesive properties, especially the low VOC-content, can be found in the use of NOVARES® LS 500 there is sufficient scope with other resin mixtures for individual combinations.

Summary

A domain for the use of aromatic C_9-hydrocarbon resins is the formulation of EVA-based hot melt adhesives. Unique tailor-made C9 hydrocarbon resins with light colour, low melt viscosity and unique compatabilities are available. They should be looked at for the development of new hot melt adhesives for paper and packaging, woodworking and graphic arts.

There is a tendency toward light-coloured aromatic hydrocarbon resins. It was shown that light-coloured fully aromatic C_9-hydrocarbon resins can be produced with Gardner colour of about 2 without hydrogenation or using only pure monomers.

Additionally it is possible to reduce odour to a distinctly lower level using modern technology in hydrocarbon resin production.

A rather new application for non-reactive aromatic C_9-hydrocarbon resins is the field of reactive hot melt systems. Due to numerous possible combinations of the different copolyesters both nonpolar as well as polar-modified aromatic C_9-hydrocarbon resins are in use.

Last but not least low VOC water-borne adhesives can be produced by using special aromatic liquid C_9-hydrocarbon resins.

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